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The Design, Activation and Selective Transformation of Organometallic Compounds into Common and Exotic Materials

by

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Submitted to NATO
*A Report to NATO based on the Advanced Research Workshop:
The Design, Activation and Selective Transformation
of Organometallic Compounds into Common and Exotic Materials*

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Future directions in Materials Chemistry research are identified based on the NATO/ONR Advanced Research Workshop "The Design, Activation and Selective Transformation of Organometallic Compounds into Common and Exotic Materials." Specific problems and research needs in the fields of : (1) Premetallic and preceramic organometallics; (2) CVD precursors; and, (3) Sol-gel chemistry are discussed. Fundamental problems at the interfaces of chemistry, physics, and materials science are also considered.

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A Report To NATO Based On The Advanced Research Workshop

The Design, Activation and Selective Transformation

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Introduction

The tenor in materials science and engineering has changed notably over the past two decades. Prior to the early '60's, the major fields of focus in materials science were confined, for the most part, to the study of ceramics, metallurgy and polymers. Moreover, research in these fields tended to proceed without mutual interaction and to emphasize characterization of the physical and mechanical properties of materials as well as refinement of standard processing techniques.

In the past two decades, the demands for: (1) high performance composite materials with high strength-to-weight ratios for aerospace applications, (2) more energy efficient/economical materials synthesis and processing technologies, and (3) new, high resolution, fabrication methods for microelectronics applications have forced materials science and scientists into new areas of focus that include a marriage of the once independent disciplines.

Materials science is headed towards an era where the scientist must consider the effects of atomic interactions on molecular interactions and in turn their effects on materials structure and properties at the nano- and micrometer level--he must consider the integration of scale--in developing new or improved materials. One particular area of research that has been propelled to center stage, because of the integration of scale approach, is the preparation of materials using chemical routes: materials chemistry.

A number of factors suggest that materials chemistry will play a major role in the future of materials science. Perhaps the most important factor is the concept of molecular design. In analogy to the monomer-polymer relationship of polymer chemistry, it should be possible to design molecular analogs or "building blocks" of almost any given material that can serve as a precursor to that material. Proper design will permit control of the elemental stoichiometry in the precursor and thereby control the elemental stoichiometry of the material product. For example, polysilazanes such as $H_2N-[H_2SiNH]_x-H$ have been used as precursors to Si_3N_4. Here the monomer unit, H_2SiNH, approximates the stoichiometry of Si_3N_4 and is the molecular building block. The potential value of this approach can be better appreciated if we consider that clays are the original preceramic materials and the constraints of design have

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been established by nature. That is, little of the diversity available via organometallic chemistry is available in clays.

The potential processing advantages materials chemistry offers provide a second factor. Molecular design permits the synthesis of tractable precursors, of known elemental stoichiometry, that can be processed at low temperatures, as one would process organic compounds (e.g. organic polymers), and only after the final shape is obtained is the precursor transformed into a finished, shaped ceramic (metal alloy, semiconductor, superconductor, etc.) piece by pyrolysis and/or sintering. By comparison, many ceramics and metallurgical processing techniques in use today are both equipment and energy intensive at all stages of processing.

In the same vein, a designed precursor that is malleable permits one to obtain shapes, using polymer processing methods, that are obtained with difficulty or not at all using standard industrial ceramics processing techniques. Thus, tractable precursors can be used to form ceramic (alloy, semiconductor,etc.) films, laminates and fibers.

Materials chemistry offers several thermodynamic advantages over current processing methodology, in addition to low temperature processing. Typical ceramics and metallurgical processing technology relies on solid state or melt reactions to obtain particular materials and/or phases. Appropriately designed molecular precursors will normally have chemical bonds between the elements desired in the final product. Therefore, the energy required to convert the precursor into the final product will be less, by the energy of those chemical bonds, than the energy required to produce that same product via solid or melt reactions. The same conclusion can be reached if we consider the energy required to cleave metal-ligand bonds in organometallics. The majority of these bonds will break at 400-500 °C or lower. It follows that almost any type of material can be formed from an organometallic precursor at temperatures below 500°C.

It is important to recognize that phase thermodynamics, control of grain size or microstructure, or complete densification may still require high processing temperatures. However, these should still be lower temperatures and/or shorter times than required by standard processing because the intimate (molecular) mixing normally obtained using precursors will mean that diffusion distances will be much less than

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under standard processing conditions.

If it is possible to prepare materials at temperatures well below those normally used industrially, then other potential benefits are conceivable. For example, the relatively high reaction temperatures required by many of today's materials processing technologies make it difficult or impossible to obtain specific phases for a given material because kinetics and/or thermodynamics dictate against their formation. Low temperature processing with designed organometallic precursors could permit one to escape this thermodynamic or kinetic control and provide entrée into rare or novel phases (see section on CVD). The same arguments suggest that low temperature processing will provide access to entirely new materials that are not thermodynamically stable under standard processing conditions.

The potential benefits of materials chemistry, as suggested above, overlap and in fact depend on the sciences of chemistry, physics, materials, engineering and biology. In order for these benefits to be realized, it will be necessary to identify and integrate the scientific and technical objectives of these fields into materials chemistry research efforts. The Advanced Research Workshop was organized with this end in mind.

The specific goals of this workshop were to promote discussions between experts in the various disciplines aligned with materials chemistry. These discussions were intended to identify the scope and potential rewards of research efforts in the development of: (1) designed precursors to common and exotic materials; (2) methods of selectively transforming these precursors in high yield to the desired material, (3) methods of characterizing the final products, and (4) potential spinoffs--new areas of research.

Because of size limitations, the workshop was limited to four focus areas; framework sciences, preceramic polymers, chemical vapor deposition (CVD) and sol-gel processing. The intent of the framework sciences section was to set the stage for the remaining focus areas by illustrating the types of technologies and sciences that can contribute and draw from materials chemistry. This section consisted of a set of papers from diverse fields ranging from theoretical inorganic chemistry to heterogeneous catalysis to hard metal processing.

A discussion session followed each focus area. The object for each

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session was to identify specific research and technical problems requiring resolution and relate them to the general theme of the conference. Each participant was asked to write a 1-2 page paper discussing what he thought were the most important problems identified both in his area of specialty and in general. These papers have been melded by the discussion leaders to give the overview presented below.

Framework Sciences

In order for materials chemistry to be applied successfully to processing problems extant in materials science, we must first deal with those problems that exist at the most fundamental levels. These are the problems of theory, molecular thermodynamics and kinetics. The results of these efforts will permit the development of detailed synthetic guidelines for organometallic precursors and their subsequent application to materials processing.

Theoretical Efforts

One of the main problems in the area of theoretical calculations actually arises simply because of differences in terminology. For example, the chemist's Jahn-Teller effect is the physicist's Peierls distortion. It appears that the time is right for the introduction of general terminology across the board or at least exchanges between the various disciplines.

Another problem area that affects all levels of research, not just the theoretical side, is the investigation of materials at the macroscopic level versus the molecular level. Theory in chemistry has generally attempted to explain phenomena and predict at the molecular level. Only recently has it been applied to understanding the physical and extended electronic behavior of macromolecules and hard metals. In general, theoretical studies in the other disciplines have been directed towards bulk physical and electronic properties. It is likely that research at the interface between these two approaches will be extremely fruitful.

Several areas that could profit from theoretical studies at both the molecular and macromolecular level include:

- What defines the size of the smallest single magnetic domain? Why does the size of the smallest domain differ with different metals or magnetic ceramics? What kind of novel properties can one expect for particles that are on the same order of magnitude or just slightly smaller than the size of a domain wall?
- When does a large metal cluster compound start behaving like a small metal particle? Is the change smooth or abrupt?
- How does metal particle size affect the catalytic behavior of heterogeneous catalysts? What are the minimum number of metal atoms that can function as a single catalyst site or function as the bulk metal?
- Why do thin films act differently from the bulk material and at what thickness does the transition take place and why?

Many more problems of this nature will require theoretical studies at both the molecular and macromolecular level. There is clearly a need for interactions of theorists in all disciplines.

Molecular Kinetics and Thermodynamics

Physical chemists and chemical physicists have developed detailed kinetic and thermodynamic data on the formation and cleavage of carbon-carbon and carbon-heteroatom bonds. These data have enabled them to establish absolute bond dissociation energies and reaction rates for a large number of organic compounds and a broad spectrum of organic reactions. By comparison, very little data are available concerning the kinetics and thermodynamics of bond formation and cleavage for organometallic and inorganic compounds. Absolute bond dissociation energies for metal-ligand bonds in organometallic compounds are difficult to find and often incorrect.

As amply illustrated below, the future of materials chemistry processing depends on the existence of detailed knowledge of the thermodynamics and kinetics that control the reactivity of organometallic and inorganic compounds. Therefore, it is imperative that researchers and funding institutions recognize the immense value to be gained from work in this area.

Premetallic Design Principles

Despite the paucity of explicit bond dissociation energies (BDEs) for organometallic compounds, there is sufficient qualititative knowledge, when coupled with the extensive literature on organometallic reaction pathways, to permit formulation of useful precursor design principles. Because the physical and chemical properties desired in precursors to hard metals, ceramics or semiconductors (especially for CVD applications) differ considerably, different constraints are placed on the design of precursors to each material type. In this section, we will discuss general design principles and emphasize the preparation of hard metals such as metal carbides and nitrides using "premetallics". A premetallic is defined here as any organometallic precursor that contains a transition, lanthanide or actinide element and provides non-oxide products on pyrolysis. Design principles for preceramic polymers and CVD precursors will be discussed in the appropriate sections below.

The following synthetic guidelines are based on several simple assumptions. One such assumption is that for the same metal, the BDE for a metal-carbon single bond is less than for an alkylidene or metal-carbon double bond, which in turn is weaker than an alkylidyne or metal-carbon triple bond. A further assumption is that metal-oxygen and metal-halogen (M-F and M-Cl in particular) BDEs are typically greater than metal-carbon single bonds for the same metal. A third assumption is that multiple bonding, as it occurs in metal clusters, enhances the likelihood that cluster integrity will be maintained during pyrolysis. These assumptions require experimental validation.

A related problem, also requiring experimental justification, concerns our ability to make across-the-board comparisons of the high temperature reactivity patterns of like ligands with different metal centers (e.g. M-Et). Because absolute values for most M-C BDEs are unavailable, attempts to compare high temperature reactivity patterns between complexes of different transition metals is very difficult at best and valid extrapolations to the lanthanide or actinide metals would seem even less feasible.

The design principles set out below must be considered in light of these significant drawbacks. The object of this report is to encourage researchers to solve these problems and thereby confirm or modify the

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following principles.

Macromolecular Criteria

In order for a precursor to be useful, it must have certain macromolecular properties. These include tractability, low volatility (except for CVD purposes), high metallic yield and, if possible, thermal and environmental stability.

Tractability is required so that shaped forms of the precursor can be prepared.

Low volatility permits the precursor to retain its final shaped form with only limited loss to the environment during pyrolysis.

High metallic yield minimizes the volume changes that occur on pyrolytic conversion of the precursor to the ceramic product.

Stability determines precursor handling and processing methods and controls the utility of specific types of precursors.

These macromolecular properties play a major role in determining the molecular design of precursors.

Molecular Criteria

The criteria for design of molecular units or building blocks for precursors must stay, in general, within the bounds set by the macromolecular criteria; however, synthetic demands and molecular design criteria often force a compromise as we will illustrate below.

The objectives that must be met by molecular design include control of: stoichiometry, ligand type and ligand content, bonding modes, and monomer structure. As with the macromolecular criteria, the validity of the molecular criteria presented below has not been substantiated experimentally. Testing these criteria represents a challenge to the synthetic chemist and the materials scientist.

Stoichiometry-- Because transformation of the precursor to product must lead to a desired material with a defined composition and phase, the elemental makeup of the precursor must closely approximate that of the product. If pyrolysis is conducted in a reactive atmosphere containing one of the elements desired in the final product then strict control of stoichiometry is not necessary.

Ligand Type--Three macromolecular criteria, and the stoichiometry

criterion limit the types of ligands that can be used in precursors. The need for a tractable precursor (liquid, soluble, meltable or malleable) places some constraints on ligand types. A meltable precursor implies that the ligands impart sufficient thermal stability to permit melting to occur. In addition to thermal stability, many applications will require ligands that impart oxidation and moisture stability. The need for high ceramic yield constrains the size and number of extraneous ligands (those present only to provide stability and tractability) that can be used to those with low formula weights, because these same ligands must be lost upon pyrolysis. Finally, the need to approximate product stoichiometry will influence the types of ligands that can be employed effectively in the precursor.

Ligand Content--The relative thermodynamic stability of all the potential ceramic products that could arise from reactions of the various elements in the ligands and the metal will control product selectivity in many instances. Thus, the elemental composition of the ligand will play a role in precursor design.

The hard metals are usually carbides (e.g. WC, Mo_2C, TiC, HfC), nitrides (e.g. TiN, VN) and borides (e.g. TiB_2) These same metals form extremely strong bonds to oxygen and halogens. Consequently, oxygen and halogen containing organometallics are not likely to be useful precursors to hard metals because they are expected to form metal oxide or halide products upon pyrolysis.

Bonding Modes--The presence of direct bonds between the metal and the element(s) desired in the ceramic product offer the greatest opportunity to selectively form that product. It seems likely that double and triple metal-element bonds will further enhance the opportunity to form the target ceramic. In the case of tungsten carbide precursors, species containing double (W=CHR) and triple (W≡C-R) metal carbon bonds are known and are potential candidates for tungsten carbide. Unfortunately, these very strong bonds are quite reactive, thus they may well disappear during pyrolysis thereby diminishing any potential advantage they might offer initially.

Metal cluster metal element multiple bonds are a viable alternative to the mononuclear metal-element multiple bonds. Tractable organometallics of the general formula: L_xM_4C, L_xM_5C and L_xM_6C, where M can be Fe, Ru, Os, Rh etc, and L = CO are known and are potential

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carbide precursors. Related complexes where the carbon is replaced with nitrogen or boron are also known and offer the potential to prepare the respective nitrides and borides.

If the carbide atom at the center of the cluster is the only good source of carbon in the molecule, then these precursors are carbon deficient because the metal:carbon stoichiometry of most of the common carbides usually ranges 1:1 to 3:1. Thus, there is a need to synthesize new types of carbide clusters perhaps on the order of the binuclear acetylene complexes illustrated below which offer the appropriate stoichiometry and are known for many metals.
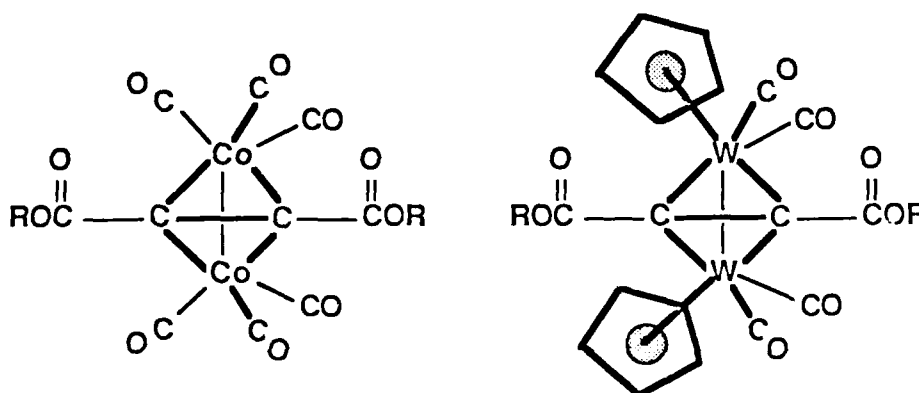
Monomer Structure--The design of the monomer unit must follow all of the macro- and molecular design criteria. In addition, it must have chemical reactivity that permits polymerization to tractable oligomers and polymers. This latter requirement represents a largely unexplored area of organometallic chemistry whose value will become increasingly important as materials chemistry develops as a field. Although several books have now been devoted to the synthesis of organometallic polymers, in general the approach has been to attach polymerizable organic moieties. Little work has been invested in the development of mechanisms whereby one obtains the metal in the polymer backbone. The opportunities for study in this area are exceptional. One can envision the development of new metal-metal bond forming reactions via catalysis as is now occuring for the synthesis of polysilane and polysilazane preceramics. An additional possibility includes the development of organometallic analogs of organic condensation reactions.

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Catalysis

Materials chemistry can play three separate roles in the area of catalyst design and preparation. It can be used as a means of: (1) controlling the shape, size and elemental makeup of the catalyst particle; (2) controlling the spatial distribution of the particle on the support surface and, (3) preparing novel supports for heterogeneous catalysts.

The typical industrial heterogeneous catalyst was developed by empirical studies followed by detailed refinement. For each catalytic process, catalyst refinement means optimizing catalyst particle size, particle distribution on the support surface and method of activation. The suppport is also optimized as to type, pore size and gross shape (ie. powder, pellet etc).

The typical catalyst particle contains many thousands of metal atoms, but only those at the surface of the particle are active. The remaining atoms, buried within the bulk of the particle, are essentially wasted except perhaps for an electronic contribution. The particle size *distribution and its distribution on and in the support are often only* crudely controlled by the method of impregnation and the pore size and distribution in the support. Fine control of all these factors will provide more effective, reliable catalysts for known processes and will facilitate the development and screening of new catalysts.

Materials chemistry is potentially a very valuable approach to catalyst design and preparation because it should provide the necessary fine control. The synthesis of catalyst particles by organometallic chemistry offers the opportunity to completely design the particle at the molecular level and optimize not only the use of metal but possibly the arrangement of metals in the particle and the use of specific promoters (e.g. alkali metals are often used as promoters).

It is now possible to design and routinely synthesize small polynuclear (and polymetallic) organometallic cluster complexes of known size, configuration and elemental makeup. Moreover, their chemical reactivity and thus the catalyst activation temperature, is to some extent controllable. In theory, it should be possible to synthesize an organometallic cluster complex that, when devoid of supporting (extraneous) ligands, can function as a single catalyst site, if properly

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placed on an inorganic support.

Although a number of research groups have made significant progress in catalyst design and synthesis using this approach, several very key problems need to be solved to evaluate its true potential. Perhaps the most important questions that remain unanswered are as follows:

- When does the catalytic behavior of a supported metal cluster compound approach that of a small metal particle? Is the change in catalytic behavior, if any, smooth or abrupt?

- What is the minimum number of metal atoms that can function as a single catalyst site?

- What reaction mechanisms can be used to facilitate fixing or "surface confining" the metal cluster/catalyst precursor on the surface?

- What reaction mechanisms can be used to facilitate catalyst activation?

The answers to these questions will differ for each catalytic reaction but, more important, is the need to search for these answers. The academic value of such a search is evident; the potential benefits to the multimillion dollar chemical and fuel processing industries which rely heavily on catalysis, could also be considerable.

Although it is now possible to synthesize a great variety of clusters with different metals and different nuclearities, few methods have been developed whereby organometallic clusters can be fixed rigidly to inorganic supports without decomposing to mononuclear species or becoming mobile during mild heating. New methods of fixing or "surface confining" clusters are needed so that the cluster can be decomposed (activated) intact under mild conditions. In this way, not only are the cluster size and configuration well defined, it should also be possible to define the exact metal-support interactions and the spatial/surface distribution of the clusters. These areas offer many opportunities to develop new science and new commercially important catalysts.

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Design and synthesis of catalyst supports is an area where materials chemistry has excelled. Zeolite synthesis is a major field of study in chemistry. The potential in this area is still relatively untapped because numerous materials possibilities are available outside the realm of alumina or silica supports. This is especially true for non-oxide materials where surface area, surface composition and electronic effects are almost unknown. The use of preceramic polymers offers the opportunity to make novel, high surface area nonoxide supports (see next section). Additionally, the sol-gel process (see below) offers some novel opportunities for support development.

Preceramic Polymers

For the purposes of discussion, we define preceramic polymers as being composed solely of main group elements. This requirement changes many of the design principles described above for premetallics because many of the bonding interactions possible with metals are not available with the main group elements. In this section, the discussion will be confined to polymeric precursors. The chemical vapor deposition of ceramic materials (including semiconductors) will be discussed in the section on CVD.

The four major problem areas in preceramic polymers research include the need for: design principles, useful synthetic approaches, pyrolysis guidelines, and methods of analysis to characterize the often amorphous ceramic products. The research needs in each area are highlighted in the following sections.

Design Principles

To develop design principles for preceramic polymers, we must first establish what properties define a "useful polymer" and a "useful preceramic". Because a "useful preceramic" must first be a "useful polymer", we begin by discussing polymer properties.

Polymer Properties

We use the term "useful polymer" to denote a polymer with rheological properties that permit it to be processed/shaped. Because

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different applications (e.g. fiber spinning, coating, etc.) require different rheologies, synthetic control of rheological properties is desirable. For example, the literature suggests that polymers have to satisfy a complex set of rheological requirements to be spinnable. This traditionally includes sufficient chain entanglement to provide the self-support necessary to allow drawing from a melt or from solution into a non-solvent. Otherwise, the polymer must be extruded, which limits the mechanical properties of the resulting fiber. Experimental results indicate that the minimum M_n necessary to obtain chain entanglement is of the order of 20,000 daltons. By comparison, high molecular weights and chain entanglement are not necessary in a preceramic used for coating applications. However, it is necessary to have a well-defined viscosity and good wetting characteristics.

On a qualitative basis, these traditional concepts provide a starting point for the development of useful preceramic polymers; however, preliminary studies with preceramics suggest that these requirements are insufficient or not always applicable. Consider the fact that most preceramic polymers described in the literature in the last 10 years have M_n = 2,000-4,000 D. The chain entanglement requirement of $M_n \approx 20,000$ D, suggests that it will be impossible to spin fibers from these polymers. However, Nicalon, a 10μm diameter silicon carbide based fiber, has been on the market for over 5 years and is produced from a polycarbosilane of Mn ≈ 2,000 D. How is this possible and why don't the traditional concepts hold up? The answers to these questions point to a number of important weaknesses in polymer theory and suggest potentially fruitful areas of research.

We must consider that the end use of the preceramic is not as a preceramic fiber, but as a ceramic fiber. There is no indication that the mechanical properties of the preceramic fiber in any way influence the mechanical properties of the ceramic product-also a fiber. It may be sufficient to spin (or extrude) a preceramic fiber that can maintain its integrity during pyrolysis. Almost all research on spinning fibers of traditional polymers has been directed towards the production of high quality (high modulus, high tensile strength etc.) fibers rather than a fiber that barely holds together.

Preceramic Properties

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The two polymer properties necessary for a "useful preceramic" include latent reactivity and high ceramic yield.

Latent Reactivity--Before the shaped preceramic can be transformed into a ceramic product, it must first be rendered intractable (infusible) prior to pyrolysis. This intermediate stage requires that the preceramic have "latent reactivity" so that following processing it can be cured or "fixed" to limit the extent of physical deformation that will occur during pyrolysis. Latent reactivity usually means that inherent within the polymer structure is some chemical reactivity that permits the polymer to be heavily crosslinked after it has been shaped. It is preferable that the crosslinking reaction also lead to loss of extraneous ligands.

The area of preceramic polymers is too new for there to be significant literature on typical inorganic crosslinking reactions. Indeed, the need for general methods of crosslinking organometallic polymers can be extended to include the need for new types of bond forming reactions for the synthesis of organometallic polymers. Thus, the development of new organometallic bond forming processes that link metal centers represents an important objective in the field of materials chemistry.

High Ceramic Yield--The transformation of a preceramic into a ceramic material requires the selective removal of the extraneous ligands without removing the ceramic forming elements or ligands. The primary problems associated with the transformation process derive from the volume and density changes that occur during pyrolysis. The typical ceramic is substantially denser than its precursor; consequently, there will be a large change in volume as the ceramic product evolves. This volume change becomes more significant if some part of the elements desired in the ceramic product volatilizes instead of forming ceramic product. This lowers the overall ceramic yield, magnifies the volume changes necessary to obtain fully dense material, and may introduce harmful discontinuities and stresses.

Design and Synthesis--General Problems

The above polymer and preceramic requirements define the pattern of design for preceramic polymers. The constraint of high ceramic yield demands that the extraneous ligands be as small as possible while still

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imparting tractability and stability. Thus, most preceramic synthetic efforts will be directed towards making hydrogen, methyl or ethyl derivatives rather than phenyl or long chain alkyl compounds.

The tractability requirement when coupled with the need for latent reactivity and control of volatility offer numerous synthetic challenges to the would-be synthesist. First, as noted for the premetallics, there are very few general bond forming reactions in organometallic chemistry that correspond to the condensation, coupling or alkene polymerization reactions known for the synthesis of organic polymers. Second, only a few limited studies have attempted to develop inorganic or organometallic crosslinking reactions for "curing" preceramics. Third, the theory of design for precursors is non-existent. Moveover, any attempts to develop theory will be hampered by a lack of thermochemical data useful for predicting likely reaction pathways. This is especially important in developing an understanding of pyrolysis processes.

Pyrolysis

The ease with which the extraneous ligands are lost and/or the ease with which the desired elements form strong bonds to the metal determine the curing time and the temperatures required for formation of the desired ceramic (or metallic) product. Perhaps the most important problems that require resolution center on the chemical process(es) whereby the precursor is converted to a recognizable ceramic product:

- What types of chemical rearrangements occur in the temperature range of approximately 200-800°C?

- Do these rearrangements lead to identifiable intermediates?

- How does one identify a persistent intermediate if it is amorphous?

- What criteria define whether the intermediate is still mostly organometallic or ceramic (metallic)?

- What thermodynamic/kinetic controls exist, at low temperature,

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that direct product formation and that are not found in standard ceramics (or metallurgical) processing?

Other questions need to be answered regarding the effects of atmosphere, heating rates and wall effects on the selectivity to ceramic product. These questions concern the chemical side of things. Other general areas of research on preceramic pyrolysis that require detailed investigation include those from the ceramist's or metallurgist's point of view. These areas include: (1) control (or lack thereof) of microstructure and microstructural evolution, and (2) control (or lack thereof) of porosity, grain size and composition. Still other questions arise from the physicist's point of view. These concern the effects processing via preceramics has on the electronic, optical and semiconductor properties of the ceramic products.

Chemical Vapor Deposition

Use of chemical vapor deposition (CVD) has grown remarkably in the last decade, so that CVD no longer represents a single technique, but a large family of related and derived processes. The whole area can be classified conveniently under a number of non-exclusive headings, by considering:

(i) The scale of operation

(ii) The intended application of the product

(iii) The nature of the precursor(s)

(iv) The deposition conditions

(v) The nature of the product (including composition)

Examples will be drawn particularly from topics covered in talks and discussions at the Workshop.

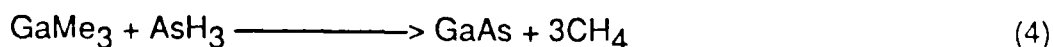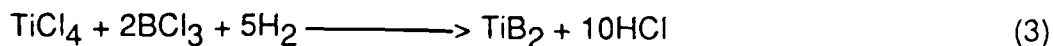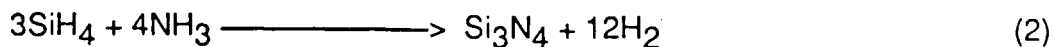## Scale of Operation; Intended Product Application

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Factors (i) and (ii) above are closely related. There is a clear distinction between large-scale processes used to form protective layers on engineering components and processes used to manufacture thin films in VLSI electronic devices. The first category typically uses large reactors, and the precise composition and purity of the relatively thick layers produced are not too critical. The second category, however, must yield thin films of extreme purity, with meticulous adherence to strictly-defined conditions. Note, however, that the scale of the second category is tending to increase, with reactors that can accommodate large banks of substrate plates.
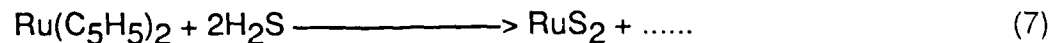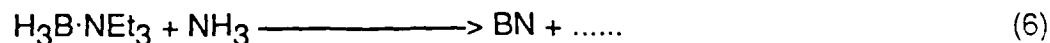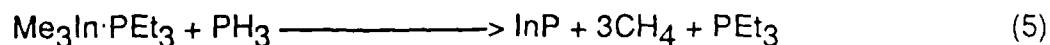
The Nature of the Precursors

Here, a considerable increase in sophistication can be seen. Some of the earliest laboratory studies of CVD used just one simple compound: obvious examples are the pyrolysis of SiH_4 and of metal carbonyls such as $W(CO)_6$. The first of these reactions has received particular attention: many theoretical, kinetic, compositional and applied studies have been carried out (although aspects of the process are still unclear). Recent examples use mixed-metal carbonyl precursors to give a bimetallic thin film, e.g.:

$$HFeCo_3(CO)_{12} \longrightarrow FeCo_x + \ldots \qquad (1)$$
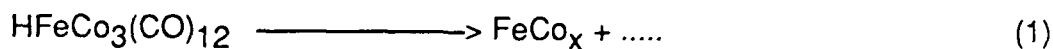
Another class of reactions involves mixtures of two or more volatile precursors: these react with each other at some stage in the CVD process, producing a solid product (deposited on the substrate) and one or more volatile products (which are either presumed inert or rapidly removed). Some examples include:
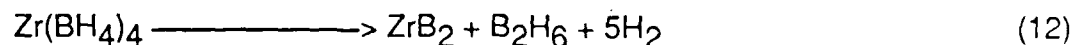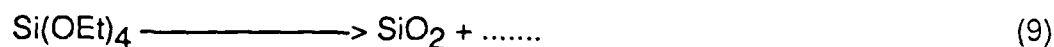
$$3SiH_4 + 4NH_3 \longrightarrow Si_3N_4 + 12H_2 \qquad (2)$$

$$TiCl_4 + 2BCl_3 + 5H_2 \longrightarrow TiB_2 + 10HCl \qquad (3)$$

$$GaMe_3 + AsH_3 \longrightarrow GaAs + 3CH_4 \qquad (4)$$

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$$Me_3In \cdot PEt_3 + PH_3 \longrightarrow InP + 3CH_4 + PEt_3 \qquad (5)$$

$$H_3B \cdot NEt_3 + NH_3 \longrightarrow BN + \ldots \ldots \qquad (6)$$

$$Ru(C_5H_5)_2 + 2H_2S \longrightarrow RuS_2 + \ldots \ldots \qquad (7)$$

Straightforward H_2 elimination (reaction 2), co-reduction of halides (reaction 3), and alkane elimination (reactions 4 and 5) are all featured; reactions 4, 5 and 7 are examples of so-called metal-organic CVD (MOCVD) where one or more precursors contains M-C (sometimes M-OR or M-NR$_2$) bonds. The use of adducts as precursors in reactions 5 and 6 should be noted: they are often easier to handle than the uncomplexed precursor, and may confer other benefits (see section on nature of products).

Finally, precursors have been developed that already contain the bond type needed in the the deposit; these have been termed prevenient precursors, and are often valuable in defining the stoichiometry of the product. One such group of compounds has been developed by the late Professor G. Constant's group for deposition of III-V materials:

$$(R_2GaPR'_2)_3 \longrightarrow GaP + \ldots.. \qquad (8)$$
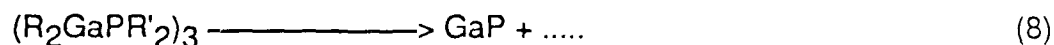
Others have been used to produce thin films of SiO_2, mixed oxides, silicides and borides:

$$Si(OEt)_4 \longrightarrow SiO_2 + \ldots \ldots. \qquad (9)$$

$$BaTi(OR)_6 \longrightarrow BaTiO_3 \ldots \ldots. \qquad (10)$$

$$(H_3Si)_2Fe(CO)_4 \longrightarrow \beta\text{-}FeSi_2 + 3H_2 + 4CO \qquad (11)$$

$$Zr(BH_4)_4 \longrightarrow ZrB_2 + B_2H_6 + 5H_2 \qquad (12)$$

Note that reaction (10) has potential for the preparation of thin films of mixed-oxide superconductors: reaction (11) produces a low-temperature phase that is not easy to make in other ways. Designing these prevenient precursors offers the greatest challenge to the chemist's

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ingenuity.

The Deposition Conditions

Reaction conditions have been varied widely in empirical attempts to optimise the nature of the product. Different geometries have been tried, in order to produce depositions of even thickness; pressure is sometimes near atmospheric, sometimes reduced (10^{-1} - 10^{-3} torr), and recently U. H. V. conditions have been explored, with very long mean free paths. Usually, the reactions are thought to be essentially heterogeneous, occurring either on the substrate surface, or just above it. But there is evidence that, in some cases, preliminary homogeneous reactions occur in the gas phase, and are significant in determining the nature of the solid deposit.

Whilst most CVD processes are still thermally induced , there is increasing emphasis on variants such as plasma-enhanced or laser-assisted CVD. Often a particular deposition will occur at lower temperatures if additional excitation is provided via a glow discharge, as with the deposition of diamond or amorphous silicon; such excitation is essential if high-quality films are to be formed. Room-temperature photolysis-only experiments have also been reported. While de-focussed laser beams produce general deposition, focussed beams can produce circuit elements of < 1μm width, and this offers the potential of writing circuits on a suitable substrate by a laser beam.

Further diversity arises in connection with carrier gases. Sometimes the precursor is injected on its own, sometimes hydrogen or oxygen act both as reactant and carrier gas, and in other cases an "inert" carrier gas such as argon is present in large excess. In the last case, however, the carrier gas atoms probably play an important role in activating precursor molecules by collisions.

The Nature of the Product

Compositional studies are crucial, and a wide range of physical techniques is commonly used to determine the phases that are present, phase homogeneity, composition/depth profiling, and the nature of the thin film-substrate interface. These techniques include XRD, electron

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microprobe analysis, Auger spectroscopy, LEED, and Rutherford back-scattering. Adventitious oxygen, carbon, and nitrogen are often found as contaminants of films, especially on the surface or at the substrate interface, unless great care is taken to purify all reactants and carrier gases. Carbon, in particular, can be harmfully incorporated because carbon-containing ligands in the precursor have not been removed cleanly.

Deposits can be amorphous, polycrystalline, or essentially single crystals, depending on the precise conditions and the nature of the precursor and substrate. Each of these forms finds specific application in microelectronics technology. Also the deposit structure, if crystalline, may be incommensurate with the lattice plane corresponding to the substrate surface, or it may match it more or less precisely. The latter situation, epitaxial deposition, has been studied especially intensively. In particular, work in the III/V area has been outstandingly successful: it is now possible to grow more than 40 epi-layers of different compositions, with constant thicknesses of some tens of angströms, by MOCVD on a single substrate. The use of Group III adducts as precursors can often help in forming good epitaxial deposits. There has also been much study of II/VI systems, mixed-oxide systems, and heteroepitaxy on silicon (including mixed Si-III/V systems).

CVD Conclusions

Inevitably, attention at the Workshop was centered on microelectronics applications, since it is here that organometallics will make the greatest impact. MOCVD is still to some extent an art form, and needs much scientific underpinning. Key areas for future work include:

- Clever syntheses of new organometallic precursors, especially prevenient types.

- Studies to identify organic groups that leave precursors cleanly, and thus avoid carbon contamination.

- Studies of new deposition conditions, especially for precursors of low volatility.

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- Theoretical/experimental studies of deposition mechanisms.

- Development of rapid and precise characterization techniques to determine the purity and homogeneity of deposits.

- Studies of composition/structure/electrical properties correlations, so that rational targetting of required phases for particular applications becomes possible.

Clearly, to reach these goals will require close collaboration between solid state chemists and physicists, theoreticians, materials scientists, and synthetic organometallic chemists.

Sol-Gel Processes

The sol-gel process offers new approaches to the preparation of oxide materials. It involves the use of molecular precursors, mainly alkoxides. A macromolecular network forms when the precursor hydrolyzes and undergoes condensation reactions. Most of the reactions occur in the liquid phase around room temperature; therefore, homogeneous multi-component systems can be obtained easily by mixing the corresponding solutions. Chemical control of the inorganic polymerization reaction can lead to "tailor-made" materials such as linear polymers of monodispersed powders. Chemical control of the viscosity of the gel state permits film deposition via dip-coating or fiber drawing.

The number of researchers working on sol-gel processing has increased rapidly over the last decade. However, true mastery of the sol-gel process will require input from both the academic and industrial sources. The major problem areas in sol-gel research include the need for:

- A more complete understanding of the inorganic polymerization processes.

- Control and comprehension of the phenomena of aggregation and gelation.

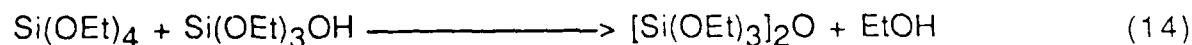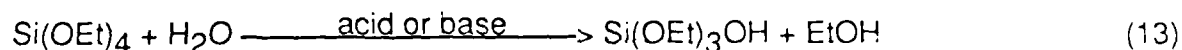- Transformation of the gel into a dense glass or ceramic material.

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• Extension of the sol-gel process to non-oxide materials and mixed
metal polymers.

Inorganic Polymerization Chemistry

The mastery of materials obtained by sol-gel processing will not
truly be realized until we develop a complete understanding of the
chemical reactions that come into play. We find ourselves in a situation
similar to polymer chemists several decades ago. We must develop both an
experimental and a theoretical understanding of inorganic polymerization
as it occurs in sol-gel processing.

At present, most sol-gel research directed towards elucidating
reaction mechanisms has focussed upon the formation of silica, SiO_2. In
particular, ^{29}Si NMR has been shown to be of great value in documenting
the first steps in alkoxysilane hydrolysis and condensation, e.g. reactions
(13) and (14). X-ray absorption techniques (XANES, EXAFS), provide a body

$$Si(OEt)_4 + H_2O \xrightarrow{\text{acid or base}} Si(OEt)_3OH + EtOH \qquad (13)$$

$$Si(OEt)_4 + Si(OEt)_3OH \longrightarrow [Si(OEt)_3]_2O + EtOH \qquad (14)$$

of information about the evolution of species during the course of chemical
reactions (changes of coordination, oligomerization). In our opinion, major
efforts must occur in three areas:

• Detailed experimental studies must be made to correlate
structure with reactivity from both a mechanistic and kinetic
standpoint. This will provide a vast ensemble of information
which can serve as the basis to establish general principles.

• These results can be used to extend structure/reactivity studies
to systems other than SiO_2. Such systems include Al_2O_3 and TiO_2
as well as mixed-metal oxides such as mullite.

• Simple theoretical models must be developed that permit one to
rationalize the above ensemble of observations and extract

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quantitative data concerning specific hydrolysis or condensation reactions that occur during sol-gel processing.

Control and Comprehension of Aggregation and Gelation Phenomena

Chemical principles can be used effectively to describe the initial events that occur during the first stages of polymerization. However, after a certain degree of condensation has been obtained, physico-chemical phenomena that affect the processes of aggregation and gelation begin to play a role in the overall process. These phenomena determine the outcome of the sol-gel process. They control the processes that permit one to obtain monodisperse powders. They regulate the viscosity of the gel and thereby control the conditions for forming films or fibers.

Considerable progress has been made recently to understand these phenomena, particular through analysis of the data obtained during small angle x-ray scattering (SAXS and SANS) studies of fractal geometries. Fundamental studies now permit these data to be simulated entirely by computer. Aggregation is both difficult to measure experimentally and difficult to describe theoretically. Yet, its understanding is necessary because aggregation is a necessary step in the transformation of a chemical precursor into a material.

Transformation of a Gel into a Material

The transformation of a gel into a material constitutes the last stage in the sol-gel process. It is a two step operation, drying and densification, which results in the final material product. The procedures employed will depend, obviously, on the type of product desired: monolithic glass, monodispersed powder, fiber or film. Theoretical studies of both steps are ongoing. However, drying techniques continue to be mainly the result of empirical efforts. The most advanced work in this area concerns hypercritical drying for the production of aerogels. The chemical and physico-chemical reactions that occur during the formation of films by dipcoating are also beginning to receive some attention.

All of this work, which comprises a mixture of academic and applied research must be encouraged and developed.

Extension of Sol-Gel Processing to Non-Oxide Materials

The greater part of sol-gel research conducted to date concerns metal oxides and silica in particular. The sol-gel process certainly must have application to other systems. We can suggest its application for sulfides, nitrides, and even carbides. The chemistry and the precursors will be quite different from the metal alkoxides currently used for sol-gel processing of metal oxides. Work in this area requires a great deal of imagination and the examples are very few.

The metal alkoxide precursors used in sol-gel processing are typically organometallic in nature. This nature may be exploitable for the synthesis of novel mixed-metal alkoxide polymers; metal alkoxide-organic polymer (formed via an oxygen bridge) or a metal alkoxide-preceramic polymer (see above). Several reports have already appeared in the case of silicon. These polymers are totally original materials which may offer novel properties for specific applications. This type of research must be pursued and expanded for there is no doubt that the fundamentals of sol-gel processing serve as bridge between the worlds of organic polymers and ceramics.

Acknowledgements